



## PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

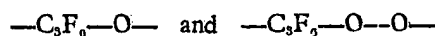
## Perfluoro-Olefin Derivatives

We, MONTECATINI EDISON S.P.A., a Body Corporate organised and existing under the laws of Italy, of 1—2 Largo Guido Donegani, Milan, Italy, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

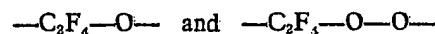
The invention relates to perfluoro-olefin derivatives which consist substantially of carbon, fluorine and oxygen atoms, and to a process for their preparation.

Chemical and thermal resistance is one of the most appreciated characteristics of organic compounds containing a high percentage of combined fluorine in the molecule. Owing to an assembly of other favourable chemico-physical properties, fluorinated compounds are of great interest and have found numerous useful applications. Fluorinated substances containing unsaturations, radicals or chemically reactive functions, for instance double bonds, carboxyl groups or their derivatives, or carbonyl groups in the molecule allow various subsequent transformations of these molecules, determine their chemico-physical characteristics, and make possible their chemical interaction with other molecules. For heat transfer, lubrication under special conditions, or electrical insulation high molecular weight fluorinated compounds which are liquid within a wide range of temperatures, having a rather limited vapour pressure and possessing the characteristics of chemical and thermal stability in a high degree, are required. For these and other applications perfluorinated compounds in general are highly suitable. In fact perfluorinated compounds in general are highly suitable. In fact perfluorinated products generally possess the highest chemical inertia and often the highest thermal stability.

The invention provides a process for the preparation of products containing



units, either alone or with



in a polymer chain which comprises subjecting perfluoropropylene or a mixture thereof with tetrafluoro-ethylene in the liquid phase to a photochemical reaction with molecular oxygen at between  $-100^{\circ}\text{C}$  and  $+25^{\circ}\text{C}$ , at a pressure between 0.1 and 10 atmospheres absolute in the presence of ultra-violet radiation.

The products of the invention have a high content of combined fluorine, practically do not contain hydrogen in the molecule, are generally liquid at room temperature and over a wide range of temperatures, stable to chemical agents and solvents, and have good dielectric, viscosity and lubrication characteristics. The process of the invention makes such compounds easily available by a simple and suitable process yielding fluorinated products having a molecular weight variable within wide limits, containing reactive functional groups, and therefore suitable for a great number of transformations. These compounds can be regarded as poly perfluoro-olefin derivatives and generally contain from 1 to 1.3 oxygen atoms per unit of combined perfluoro-olefin.

The preferred operating temperature is from  $-80^{\circ}\text{C}$  to  $0^{\circ}\text{C}$ . The preferred operating pressure is from 0.2 to 5 atmospheres absolute and generally under about atmospheric pressure. The oxygen may be fed in admixture with other gases, generally inert. The ultra-violet radiation used should have a wave length between 1000 and 4000 Å, preferably prevalently higher than 2600 Å. Alternatively a wave length lower than 2600 Å may be used and a product having an oxygen content of 1.3—2 atoms per combined perfluoro-olefin unit is

obtained which may be subjected to further U.V. radiation of the higher wave length mentioned above, or to heating up to 400°C, or both.

5 In order to define the structure of the products of the invention, for the sake of simplicity, the general formula  $(MO_x)_n$  wherein M is a unit derived from the opening of the double bond of a perfluoro-olefin,  $n$  is the  
10 average number of perfluoro-olefin units combined in the molecule, and  $x$  is an averaged value that varies from 1 to 2 will generally be used herein. When the value of  $n$  is sufficiently high that the variation in the per-  
15 centage composition caused by the presence of the terminal acid fluoride groups becomes negligible, the value of  $x$  gives an immediate indication of the ratio between the peroxy groups of the type C—O—O—C, and of the  
20 ether groups C—O—C contained in the molecule. This ratio is in effect given by the

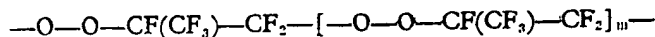
expression  $\frac{x-1}{2-x}$ , wherein  $x-1$  and  $2-x$

25 respectively represent the average values of peroxy and ether bridges associated with each unit of combined fluoro-olefin.

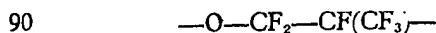
As regards the chemical composition of the new compounds of the invention, a role of  
30 fundamental importance is played by the type of U.V. radiation used for promoting the reaction. By varying the type of U.V. radiation it is possible to obtain reaction products hav-  
ing a varied oxygen content. By type of radiation we mean the distribution and the relative  
35 intensity of the radiations having different wave lengths which together compose the radiation in the reaction vessel. If the photochemical

40 reaction between oxygen and one or more perfluoroolefins is carried out under the action of U.V. radiations having a wave length between 1,000 and 3,000 Å, particularly  
45 between 1,800 and 2,600 Å, and in the absence of noticeable proportions of radiations having a wave length higher than 3,000 Å, the reaction product mainly consists of compounds  
50 having the general formula  $(MO_x)_n$  in which  $x$  has a value which is 2 or very near 2. If substantial proportions of radiations having a higher wave length, for example between 2,600  
55 and 4,000 Å are used, the reaction products mainly consist of compounds having the general formula  $(MO_x)_n$  in which the value of  $x$  is lower than 2, and the more intense the radia-  
60 tions having lower energy that is a wave length higher than about 3,000 Å, the closer  $x$  approaches 1. Thus by suitably varying the U.V. light source used for activating the  
reaction or by varying the spectrum of the radiations introduced into the reaction vessel  
in which the combination between the per-  
fluoro-olefin or perfluoro-olefins with oxygen  
takes place, the chemical composition of the  
polymeric products obtainable can be varied  
as desired between the formula  $(MO_2)_n$  and  
the formula  $(MO)_n$ .

Without pretending to formulate a hypo-  
65 thesis as to the mechanism of this reaction, we believe that the high energy radiations, such as those having a wave length between 1,800 and 2,600 Å, activate the combination  
70 of oxygen with the perfluoroolefin through a true copolymerization. In the case of perfluoropropylene this would for example lead to the formation of chains of the type:



75 which grow by continuous alternating combination of perfluoro-propylene and of oxygen. As the result a polyperoxide having the general formula  $(\text{C}_3\text{F}_6\text{O}_2)_n$  and a polymerization degree  
80  $n$  which can be as high as 100 and in which the terminal groups contain COF functions is obtained. The lower energy radiations, having a wave length, for example between 3,000  
and 4,000 Å, cause a modification in the afore-  
mentioned polymeric chains by decreasing the  
85 average number of combined oxygen atoms per unit of fluoroolefin. For instance in case of perfluoro-propylene this would lead to the formation of compounds having a limit struc-  
ture consisting of periodic



units and acid groups as chain terminals. Besides these products, there is also obtained  
a certain amount of the epoxide of the per-  
fluoro-olefin used. This modification (whereby  
95 in the limit a pure polyether and not a poly-

peroxide is obtained) is possible either during  
the same synthesis, by using U.V. radiations  
of a wider spectrum, or after the initial syn-  
thesis, by subjecting the previously prepared  
polyperoxide to radiations of a suitable energy.  
100 By passing a molecular oxygen flow through a liquid perfluoro-propylene phase kept at  
between -80°C and -40°C, irradiated by  
means of an U.V. radiation source consisting  
of a low pressure mercury-vapour generator  
105 (whose emission spectrum does not comprise substantial amounts of radiation having a wave  
length higher than 2,600 Å) a progressive  
absorption of oxygen is observed. By stopping  
the reaction after a certain time and distilling  
110 off the unreacted perfluoropropylene, a liquid  
substance having a very high viscosity, a very  
high molecular weight, for example of the  
order of magnitude of  $10^3$  or  $10^4$ , and an  
empirical composition exactly corresponding  
115 to the formula  $\text{C}_3\text{F}_6\text{O}_2$ , was obtained as the reaction product.

This substance was insoluble in the usual

organic solvents but soluble or miscible in all proportions with various fluorinated and in general halogenated liquids, such as perfluoro-propylene, perfluorocyclobutane, perfluoro-dimethylcyclobutane, and fluorotrichloroethane. The presence of functional acid groups of the type COF, was determined by both acidimetric titration and the presence of the appropriate bonds in the infrared absorption spectrum. The peroxidic composition appeared evident from the fact that this compound releases substantial amounts of iodine on contact with solutions of alkali metal iodides for example in acetic anhydride. A sample of this product was subjected, either in the pure state or in solution, for example in perfluoro-propylene, to the action of U.V. radiation having a wave length between 1,800 and 4,000 Å and it gradually transformed with a decrease in its combined oxygen content and in its oxidizing power to reach in the limit the empirical composition  $C_3F_6O$ . This composition corresponds to that of a polyether of perfluoro-propylene in which the presence of peroxidic groups is no longer detectable but which still contains acid functions at the ends of the chains. By graduating the time of this treatment, compounds having the composition  $(C_3F_6O_x)_n$  in which the value of  $x$  can be varied as desired in the range between 2 and 1, have been obtained. Analogous compounds have been obtained directly in the synthesis by using U.V. radiation of a suitable spectrum to activate the reaction between perfluoro-propylene and oxygen. For instance by using as the source of U.V. radiations a high pressure mercury-vapour generator producing radiations having wave lengths between 1,800 and 4,000 Å, products having the composition  $(C_3F_6O_x)_n$  in which  $x$  has a value which can be higher than 1 but is always lower than 2, that is to say products containing at the same time ether and peroxy bridges have been obtained. The oxygen content of these products appears to be variable as a function not only of the particular emission spectrum of the U.V. source used but also of the time of further action of the radiation of the already formed product. If compounds having, for example, the composition  $(C_3F_6O_{1.2})_n$ , obtained by the action of oxygen on liquid perfluoro-propylene irradiated with a given U.V. light source, are subjected to a further irradiation with the same source of radiation but in the absence of oxygen, they undergo a progressive modification of their composition, that is to say progressive decrease in their combined oxygen content. Not only the U.V. radiations but also the action of heat can be profitably used to transform products having a given combined oxygen content into products having a lower oxygen content and therefore a lower number of peroxidic groups in the chains. For example if liquid compounds obtained by photochemical reaction of oxygen with perfluoro-propylene, having the composition  $(C_3F_6O_x)_n$  in which  $x$  is between 1.1 and 1.9, are heated to from 50° to 400°C, they are transformed into compounds having a lower oxygen content and, in the limit, by prolonging the treatment or increasing the temperature, into compounds having the composition of polyethers of perfluoro-propylene. This treatment can be carried out under atmospheric pressure or under a pressure higher or lower than atmospheric pressure, on the perfluoro-oxygenated substances in the pure state or on their solutions or suspensions. It is therefore clear that, by the process of the invention from one or more perfluoro-olefins (M) it is possible to obtain polymeric products having the composition  $(MO_x)_n$ , wherein  $x$  can be 1 or 2 or can have any value between 1 and 2. This combined oxygen percentage can be varied as desired within the aforementioned limits by using a suitable U.V. radiation to activate the reaction between the perfluoro-olefin and oxygen or also by subjecting the same compounds to treatments such as irradiation with U.V. radiations, heating or a combination of both. These treatments which reduce the combined oxygen content in the form of peroxidic oxygen, can be carried out either on the compounds as directly obtained from the synthesis or on their derivatives, such as those obtainable by hydrolysis, salt, ester, or amide formation, or decarboxylation of the chain terminal carboxylic groups derived from terminal COF groups.

The products thus obtained present various characteristics which render them of a great interest for various possible applications. As was ascertained, when the value of  $x$  is 1 or approaching 1, in the compounds  $(MO_x)_n$  (either as obtained from the synthesis or modified by conventional chemical operations as to the nature of the terminal groups), the molecules do not contain substantial amounts of peroxidic groups and the compounds have exceptional chemical and thermal stability. For instance, if compounds of this type, deriving from perfluoro-propylene and having the empirical composition  $C_3F_6O_{1.1}$ , are mixed with molten potassium hydroxide at high temperatures (300 to 350°C), they form salts, and the acid terminal groups are eliminated in the form of carbon dioxide, they are transformed into neutral oily substances which are exceptionally resistant to heat and to chemical reactants. They can be separated by distillation into fractions having a different average molecular weight and therefore a different value of  $n$ , which have a boiling point between 100°C under atmospheric pressure and 350°C under 0.1 mm Hg or above, and a viscosity and density regularly increasing as the molecular weight increases. These substances can find useful applications as fluids resistant to heat and of chemical reactants, as lubricants for exceptional conditions of use, as

fluids for heat exchange, and dielectric insulation, as plastifiers and solvents for polymers and particularly for fluorinated polymers. Compounds of this type, even containing a substantial proportion of peroxidic groups, can find uses, both as free acids and their derivatives, as surface active agents, impregnating agents for fibres, paper, and fabrics, to give them properties of oil and water-repellency.

The products of the invention in which the value of  $x$  is 2 or approaching 2, have properties completely in agreement with their polyperoxidic nature: they decompose, even violently, under heat and have remarkable oxidizing properties; for instance they oxidize hydroiodic acid to iodine and this reaction can be suitable for a comparative determination of their peroxidic group content. These compounds can find application in the field of liquid propellants and other uses of peroxides.

The products of the invention in which the average oxygen content is between 1 and 2 atoms per combined perfluoro-olefin unit have characteristics which are intermediate between those of the polyethers and of the polyperoxides, that is the lower their oxygen content the higher their thermal stability or conversely, the higher their combined oxygen content, the higher in general their oxidizing power and their chemical reactivity.

The products of the invention have physical properties which vary between those of gaseous substances at room temperature and atmospheric pressure and those of liquid or semi-solid substances having a high viscosity and a very low vapour pressure at ordinary temperatures. These new products have a molecular weight between rather wide limits, which can also reach and exceed values of the order of 10,000 and which therefore puts at least a part of these products in the group of the macromolecular substances.

Reactions of perfluoro-olefins with oxygen leading not to degradation products due to breaking of the double bond by oxidation and consequent fragmentation, but to the formation of a wide range of compounds of high and very high molecular weight, were not known until now. It is indeed surprising that stable high molecular weight products containing oxygen can be formed by direct reaction of an unsaturated compound with molecular oxygen.

Generally, the reaction products are substances having a molecular weight at least 16 units higher than that of the perfluoroolefin from which they derive, and can reach and exceed values of the order of magnitude of 10,000. Among the products obtainable by photochemical reaction with oxygen those of lower molecular weight can be gaseous substances at room temperature and atmospheric pressure. Among the crude substances are generally present considerable amounts of epoxide of the starting perfluoro-olefin(s). The

products of higher molecular weight are colourless liquid substances of oily appearance and normally having a practically continuous distillation curve. The boiling temperature of these products can be within rather wide limits, for example, between 10°C at atmospheric pressure and 350°C at 0.1 mm Hg. Furthermore a fraction having a distillation temperature higher than 350°C at 0.1 mm Hg which has the appearance of a colourless, transparent and very viscous liquid, is often present. Generally the various fractions, which can be separated by distillation from the whole product of the photochemical reaction of perfluoro-olefin with oxygen, have a medium molecular weight and a viscosity and density continuously increasing with the boiling temperature. These fractions, however, show certain very similar chemical and physical characteristics which enables them to be considered from certain aspects, as consisting of a series of homologous products, in the first place distinguishable by a different molecular weight.

From the point of view of their chemical structure, the products which are obtained are rather complex and highly influenced by the composition of the starting mixture of perfluoro-olefins and, since the perfluoro-olefins have different reactivities in the photochemical reaction with oxygen, by the degree of conversion reached. A general characteristic of the products obtainable according to the invention is the presence in their molecule of functional groups having an acid character. The most part of these consists of acid fluoride groups,  $-\text{COF}$ . These groups reveal their presence, for instance in the infrared absorption spectrum causing a characteristic absorption in the  $5.25 \mu$  zone. In the products obtained in the reaction absorption bands in the  $5.6 \mu$  zone probably due to the presence of free  $-\text{COOH}$  carboxyl groups, are often present. They can easily be formed by hydrolysis of the  $-\text{COF}$  groups, by contact with moisture during the various treatments of the products. The presence in the products of acid terminal groups is also made evident by the behaviour of these products towards reagents, such as water, bases, alcohols, and amines which chemically interact with them. The amount or the concentration of acid groups present in certain fractions of the products can be determined by various methods for instance by titration with an alkali solution or by infrared spectrophotometry. The higher is the concentration of acid groups in the liquid products obtained from a given perfluoro-olefin by photochemical reaction with oxygen, the lower the boiling temperature of the fraction. Fractions of liquid products, as can be obtained for example by photochemical reaction of perfluoro-propylene with oxygen show equivalent weights determinable by acid-base titration, between about  $10^2$  and  $10^4$  depending upon the boiling temperatures between 20°C

- at atmospheric pressure and 350°C or more at 0.1 mm Hg. In the infrared absorption spectrum of these fractions are constantly present, besides the already mentioned absorption bands due to the presence of —COF and —COOH groups, other characteristic absorptions independent from the boiling temperature and, therefore, of the molecular weight of these products. A wide absorption is present between 7.5 and 9.2  $\mu$ , with a maximum at about 8.0  $\mu$  and other characteristic bands occur at 10.15 — 11.2 — 11.5 — 12.05 — 12.35 and 13.4  $\mu$ . In the products obtained by reacting with oxygen, according to the process of the invention, mixtures of perfluoro-ethylene and perfluoro-propylene other characteristic absorption bands are present, the position and intensity of which depend upon the initial composition of the mixture.
- The photochemical reaction between one or more perfluoro-olefins and oxygen has a very general character. In fact, it is possible to carry out this reaction in the liquid phase, in the absence of any other compound not being the perfluoro-olefin(s) and oxygen, or in the presence of a variety of liquid diluents. While the photochemical reaction between oxygen and perfluoro-olefins can be carried out under very different conditions, it has, however, been observed that when these reaction conditions are suitably varied, considerable variations in the reaction rate and at the same time in the characteristics of the products can be achieved. Generally, it has been observed that an increase of the average molecular weight of the products is obtained when adopting low reaction temperatures, high perfluoro-olefin concentrations, in the reaction zone, and reduced radiation intensities. On the other hand, a lowering of the average molecular weight of the products is obtained when the reaction is carried out at higher temperatures with limited concentrations of the perfluoro-olefins and with a high radiation intensity in the reaction zone. The preferred reaction conditions are to keep the reacting perfluoro-olefin(s) in the liquid phase and radiate the liquid phase with a source of ultraviolet light while feeding it with a gaseous stream of oxygen or oxygen diluted with nitrogen such as air or some other gaseous oxygen-containing mixture, at between —100°C and the boiling temperature of the liquid phase at the pressure adopted. In practice this temperature can reach about 25°C. In order to simplify things, under these conditions one operates preferably at atmospheric or slightly higher pressure.
- A convenient way to carry out the photochemical reaction between oxygen and perfluoro-olefins in the presence of a liquid phase is to add another compound in the liquid state under the reaction conditions to the reaction system. This diluent can be selected among various compounds which do not react to any considerable extent with oxygen under the selected radiation conditions and may or may not possess dissolving properties with respect both to the perfluoro-olefin(s) used in the reaction and to all or part of the reaction products. Compounds which can be suitable for these functions are for example the perfluoro-compounds such as perfluoro-cyclohexane, perfluorodimethyl-cyclobutane, the perfluoro-paraffins having the general formula  $C_nF_{2n+2}$ , wherein  $n$  is for instance between 3 and 12, perfluoro-cyclobutane, perfluoro-benzene, the perfluoro-amines such as tri-perfluoro-butylamine, perfluoro fatty acids having for example from 2 to 10 carbon atoms in the molecule, the perfluoro ethers having open or cyclic molecules such as perfluoro-propyl-pyrane, and the oxygenated perfluoro compounds which can be obtained according to process of the invention. Furthermore, totally or partially chlorinated compounds such as carbon tetrachloride, chloroform, methylene dichloride, methylchloroform, or chlorofluoro derivatives of methane, ethane, propane, such as those of the formulae  $CF_3Cl$ ,  $CF_2Cl_2$ ,  $CFCl_3$ ,  $CHF_2Cl$ ,  $CHFCl_2$ ,  $CF_2Cl—CF_2Cl$ ,  $CFCl_2—CF_2Cl$ ,  $CCl_3—CF_3$ ,  $CF_2Cl—CH_3$ , or  $CF_3—CFCl—CF_2Cl$  can be used as reaction medium. When a diluent used in the reaction has dissolving properties with respect to the perfluoro-olefin(s) employed, the photochemical reaction with oxygen can be carried out most simply by sending a gaseous stream of oxygen, or an oxygen-containing gas into a vessel containing the radiated solution of the perfluoro-olefin(s) in the selected solvent kept at the temperature and pressure chosen for the reaction. If under these conditions one or more of the components of the liquid phase has a considerable vapour pressure, it can be convenient to use on top of the reaction vessel a reflux condenser, kept at a low temperature so as to limit or to prevent completely losses of high vapour-pressure compounds of the liquid phase due to evaporation or entrainment with the oxygen or the other gases leaving the reactor. Under these conditions the maximum reaction temperature is the temperature at which the vapour pressure of the solution reaches the pressure chosen for the system. By varying the type of solvent used and the concentration of the perfluoro-olefin(s) in it, the photochemical reaction in the liquid phase can be carried out at a temperature also higher than the boiling temperature of the perfluoro-olefin(s) to be reacted at the pressure adopted. Some diluents which can be used in the reaction, though being solvents of the perfluoro-olefin(s) to be reacted, are not at all or only partially solvents of the reaction products. Diluents of this type are for example those of the formulae  $CCl_4$ ,  $CHCl_3$ ,  $CH_2Cl_2$ . In this case the liquid reaction products separate into two phases as the reaction proceeds and can be continuously extracted from the reaction vessel. If feeding of an equivalent

amount of the perfluoro-olefin(s) together with the oxygen is carried out simultaneously, it is possible to carry out the photochemical reaction in the liquid phase in a completely continuous way. Among the various ways of possible operation is included the use of a liquid substance being a solvent neither for the perfluoro-olefin(s) nor for the reaction products. In this case the reaction is preferably carried out by continuously sending into the radiated liquid phase a gaseous stream containing the perfluoro-olefin(s) and the oxygen in the desired ratios and by continuously removing the liquid or gaseous reaction products from the liquid phase. Various other devices such as the use of activators, photosensitizers, modifiers, and/or regulators, can be used for carrying out the process of the invention. Independently of the particular method chosen, a great number of new compounds essentially consisting of C, F and oxygen atoms, which have as main characteristic a very high chemical and thermal resistance, and moreover contain functional groups of acid nature, can easily be prepared using the process of the invention. These products consequently show particular properties and can be used for a great number of transformations and useful applications. When the molecular weight of these products does not exceed about 1000 owing to the presence of acid groups, the compounds are soluble in water and alkaline solutions, and with bases with formation of the corresponding salts, or with other organic products to yield various derivatives, for instance with alcohols to form esters, with ammonia or amines to form amides, and generally show most of the reactions characteristic of perfluoro organic acids. They can give carboxylates yielding the corresponding saturated or unsaturated compounds, when pyrolysed under suitable conditions, both in the free form and in the form of alkali metal salts.

When the molecular weight of the product exceeds about 1000, the acid character is less evident, because a longer part of the chain or residue of neutral character remains bound to each acid group. Then the products, in aqueous solution or suspension, especially when alkaline, have considerable surface-active characteristics causing the formation of emulsions which can be very stable.

The products of the invention show characteristics of solubility in common organic solvents which depend upon their molecular weight. Only the fractions consisting of products of limited molecular weight are miscible in solvents like diethyl ether, toluene, carbon tetrachloride, and acetone; the fractions of higher molecular weight are completely immiscible in these and other solvents. Solvents miscible in all proportions at ordinary or lower temperatures with the whole range of products to be obtained according to the invention are the liquid perfluoro compounds, such as the

cited perfluoro-olefins, perfluoro-cyclobutane, perfluorodimethyl-cyclobutane, and generally the perfluorinated hydrocarbon-, acid-, ether- and amine-derivatives. Also various partially fluorinated compounds, such as those of the formulae  $\text{CF}_2\text{Cl}_2\text{CF}_2\text{Cl}-\text{CF}_2-\text{Cl}$ ,  $\text{CF}_2\text{Cl}-\text{CFCl}_2$ , and  $\text{CF}_3\text{Br}$ , have good dissolving properties.

Solutions of the products according to the invention in one of the above mentioned solvents can usefully be employed in all chemical and physical treatments of the products, because by lowering the viscosity of the liquid media, they favour contact and therefore the exchange, substitution, and combination reactions with various liquid or dissolved reagents which normally are immiscible with products alone.

In the following Examples, which illustrate the invention, a quartz "Original Hanau" type Q 81 ultraviolet-ray lamp having a tubular form, a size of  $245 \times 20$  m.m. and an absorption of 70 Watt and generates a wavelength emission chiefly between 2400 and 4400 Å has been employed as source of ultraviolet radiation except where otherwise specified.

#### EXAMPLE 1

An apparatus is prepared consisting of a ball-shaped glass reaction vessel having a capacity of 1.5 litre and provided with a thermometer; and a gas inlet dipping pipe reaching the bottom, and connected with the atmosphere by means of a reflux condenser wherein a cooling mixture at  $-78^\circ\text{C}$  is put. An ultraviolet-ray lamp is introduced into the reaction vessel and by means of external cooling at  $-78^\circ\text{C}$ , 1230 g of pure perfluoropropylene are condensed in it, through the dripping pipe. While maintaining the external cooling so as to keep the temperature of the liquid between  $-60$  and  $-30^\circ\text{C}$ , the UV lamp is switched on while, by means of a circulation pump, a stream of anhydrous oxygen of 130 l/h (litres per hour) is sent through the inlet pipe dipping down to the bottom of the reaction vessel. The gas leaving the reaction vessel after having passed through the reflux condenser is washed with an aqueous potassium hydroxide solution having a concentration of 20% and then collected in a 50 litre gasometer from which, after drying, the gas is once more sucked by the pump and recycled into the reaction. An oxygen amount equivalent to that consumed in the reaction is periodically fed to the gasometer. After 28 reaction hours about 75 NI (normal litres) of oxygen have been absorbed and the reaction is stopped. The non-reacted perfluoro-propylene and reaction products having a boiling temperature lower than  $30^\circ\text{C}$  at room pressure are separately distilled off and removed from the reaction vessel. 650 g of a mixture containing 78% by weight of perfluoro-propylene and

19% of perfluoro-propylene epoxide (b.p. - 29°C) are thus obtained. 5

The remaining liquid products amount to 650 g and have the appearance of a colourless, transparent viscous oil. They are distilled without reflux and the following fractions are obtained.

Fraction	Distillation Interval	Grams
a)	30—40°/760 mm	11
b)	40—64°/760 mm	8.5
c)	50°/20 mm — 105°/20 mm	37
d)	55°/0.5 mm — 100°/0.2 mm	40
e)	100°/0.2 mm — 155°/0.2 mm	53
f)	155°/0.2 mm — 350°/0.1 mm	462
g)	residue	30

- Fractions a), b) and c), which consist of liquids having a stinging odour and develop hydrofluoric acid fumes when exposed to moist air, are put together and dissolved in 300 cc of 2 N potassium hydroxide. The aqueous alkaline solution is repeatedly extracted with a total amount of 500 cc of diethyl ether. The ethereal layer is washed (and stirred) with 100 cc of sulphuric acid having a concentration of 50%, dried over sodium sulphate and distilled over phosphorus pentoxide. After removal of the ether, 13 g of fluorooxygenated products having a boiling point between 40 and 190°C and an average equivalent acidimetric weight higher than 200 are obtained. After the extraction with diethyl ether, the alkaline solution is acidified by addition of 100 cc of sulphuric acid having a concentration of 98% and extracted with 500 cc of diethyl ether. The ether solution is distilled over phosphorus pentoxide and, after removal of the ether, 41 g of a product consisting of fluorinated carboxylic acids are obtained which have a distillation temperature between 90 and 200°C and equivalent acidimetric weights between 164 and 900. These acids show considerable surface-active properties when introduced in low concentrations into a neutral or weakly alkaline aqueous medium.
- Fractions d) and e) are put together and the product is subjected to an accurate fractionation in a rectifying column under a residual pressure of 10 mm Hg. In this way, the fraction reported in Table 1 are separated. In the same Table data relating to density, viscosity, equivalent acidimetric weight and percentage composition determined on various fractions are listed.

TABLE 1

Number of Fractions	g	Distillation interval (°C.) at 10 mm Hg	24 d 24	Equivalent acidimetric weight	Viscosity (centipoises) at 24° C.	Percentage C %	Composition F %
1	7.8	67.5 — 93.0	1.7877	497	6.4	20.62	64.1
2	8.2	93.0 — 114	1.8035				
3	8.5	114 — 130	1.8260	1044	11.0		
4	7.3	130 — 140	1.8239			20.86	67.0
5	8.1	140 — 150	1.8342	1477	15.5		
6	7.8	150 — 157	1.8352				
7	8.3	157 — 168	1.8380	2640	22.9	21.12	68.0
8	8.0	168 — 180	1.8520				
9	8.2	180 — 193	1.8517	2832	32.3		
10	8.1	193 — 208	1.8574				
11	11	108 — 225	1.8684	3150		21.22	68.3



The equivalent acidimetric weights were obtained by introducing about 0.4 g. of exactly weighed product into 25 cc of 0.1 N sodium hydroxide keeping the whole in strong agitation for 2 hours at room temperature and back titrating with 0.1 N hydrochloric acid using phenolphthalein. In the thus neutralized solution the fluoride ions present were determined with thorium nitrate. The ratio between the weight in grams of the starting product and the difference between the number of acid equivalents of the product and the number of the equivalents of fluoride ions was taken as the equivalent acidimetric weight.

The infrared absorption spectra of the various fractions are all similar one to another, presenting absorption bands in the  $5.25\ \mu$  zone and in the  $5.6\ \mu$  zone, due to the presence of  $\text{—COF}$  and  $\text{—COOH}$  groups, respectively.

The intensity of these absorption bands decreases through the various fractions as the

boiling temperature increased. Other infrared absorption bands present in all the fractions occurred in the zones between  $7.5$  and  $9.2\ \mu$  and furthermore at  $10.15$  —  $11.2$  —  $11.5$  —  $12.05$  —  $12.35$  —  $13.4\ \mu$ . Solubility tests of the various fractions in diethyl ether have shown that, while fractions 1 and 2 are miscible in all proportions with the solvent, fractions 10 and 11 are practically immiscible. The other fractions show an intermediate behaviour. All these fractions are completely miscible in all the perfluorinated solvents examined.

Fraction f) has an average density  $d_{24}$  of 1.8953 and an average equivalent acidimetric weight of about 4000. In fraction f) the following viscosities are determined at different temperatures:

temperature, °C:	24	30	40	50
viscosity, centipoises:	264	193	117	76

The infrared absorption spectrum of the product of which fraction f) consists has revealed, besides the presence of small absorptions in the zones of the  $\text{—COF}$  and  $\text{—COOH}$  groups, a wide absorption between  $7.5$  and  $9.2\ \mu$  with a maximum at about  $8.0\ \mu$ , and other characteristic absorptions in the  $10.15$  —  $11.2$  —  $11.5$  —  $12.05$  —  $12.35$  —  $13.4\ \mu$  zones.

A portion of 100 g of fraction f) was slowly introduced, with strong stirring, into 100 cc of an aqueous sodium hydroxide solution having a concentration of 30%. The white viscous mass thus obtained was repeatedly washed with water with strong stirring and then treated with 100 cc of sulphuric acid having a concentration of 98%, at  $80$ — $90^\circ\text{C}$ . The oil separated was washed with water, separated and distilled. 75 g of a rather viscous liquid product having a distillation interval between  $160$  and  $310^\circ\text{C}$  at  $0.5\ \text{mm Hg}$  was obtained having an infrared absorption spectrum completely similar to that of the product before the hydrolysis treatment except that the absorption due to the  $\text{—COF}$  groups has disappeared while the absorption due to the  $\text{—COOH}$  groups proportionately increased.

The viscosity at  $30^\circ\text{C}$  of the hydrolyzed product is 320 centipoises. Another hydrolysis operation was carried out by dissolving 10 g of the product of fraction f) in 100 cc of perfluoro-dimethylcyclobutane and treating the solution with 50 cc of water, while stirring. The organic layer was separated, dried over phosphorus pentachloride and distilled. Thus 9 g of hydrolyzed product having characteristics completely similar to those reported above are obtained. Small quantities of hydrolyzed product give rise on contact with water or an alkaline solution to the formation of a very

stable emulsion. Samples of the product of fraction f) and samples of corresponding hydrolyzed products heated in the air to  $350$ — $400^\circ\text{C}$  for a long period did not become coloured, nor give any other notable symptoms of modification.

50 g of the product of fraction f) are heated with 5 g of potassium hydroxide in the form of tablets for a period of 2 hours at a temperature of  $240$ — $250^\circ\text{C}$  at atmospheric pressure, in a 100-cc flask being part of a distillation apparatus. During this treatment the development of carbon dioxide and water vapour is observed. At the end of this treatment the contents of the vessel are subjected to vacuum distillation. About 40 g of colourless, transparent oil having a boiling interval between  $120$  and  $200^\circ\text{C}$  at  $0.2\ \text{mm Hg}$  are thus obtained. This product no longer shows an acid character, is completely indifferent towards water and alkaline solutions, and has an infrared absorption spectrum from which absorptions due to acid functions are completely absent.

The residual fraction g) has a viscosity at  $24^\circ\text{C}$  higher than 2000 centipoises, a density  $d_{24}$  of 1.9104, and shows an exceptional resistance to thermal treatment, both in air and under high vacuum, without showing any sign of modification after prolonged periods of heating at temperatures of about  $400^\circ\text{C}$ . The infrared absorption spectrum of this fraction is completely similar to that of the preceding fractions, except for the very low intensity of the absorptions corresponding to the acid groups.

Fractions f) and g) are miscible in all proportions with perfluorinated solvents such as

perfluorocyclobutane, perfluorotributylamine, and perfluoropropylpyran. On the other hand they are immiscible with the common organic solvents such as acetone, diethyl ether, tetrahydrofuran, toluene, carbon tetrachloride, chloroform, methylene dichloride, dioxan, dimethylsulphoxide, dimethylformamide, and ethyl acetate.

#### EXAMPLE 2

The same apparatus as in Example 1 is prepared, except that a glass cylindrical vessel having a volume of 0.4 litre, in which the UV-ray lamp is contained, is used as reactor. 165 g of perfluoropropylene and 200 cc of perfluorocyclobutane are collected in the

reaction vessel by distillation at  $-78^{\circ}\text{C}$ . The reaction is started by passing an oxygen stream at about 50 l/h and by lighting the UV-lamp at a temperature of  $-45^{\circ}\text{C}$ . The reaction is continued for a period of 11 hours, during which the temperature of the liquid phase gradually rises until it reaches  $-9^{\circ}\text{C}$  and totally about 18 N litres of oxygen are absorbed. Finally, perfluoro-cyclobutane the unreacted perfluoro-propylene and the products having a boiling temperature lower than  $25^{\circ}\text{C}$  at atmospheric pressure are distilled off. The residue consists of 95 g of a liquid product which gives the following fractions when subjected to distillation:

Fraction	Weight (g)	Distillation Interval
A)	11.6	25— $90^{\circ}\text{C}$ /760 mm Hg
B)	20.3	90— $160^{\circ}\text{C}$ /760 mm Hg
C)	29.2	50— $100^{\circ}\text{C}$ /0.2 mm Hg
D)	15.2	100— $150^{\circ}\text{C}$ /0.2 mm Hg
E)	12.8	150— $280^{\circ}\text{C}$ /0.2 mm Hg
F)	3.0	residue

The products show characteristics equivalent to those obtained in the corresponding distillation interval, in Example 1. The presence of a solvent during the reaction and also the higher radiation intensity have led to the formation of a product having a lower average boiling temperature.

#### EXAMPLE 3

Under the conditions of the preceding Example, 135 g of perfluoro-propylene and 340 g of carbon tetrachloride are reacted with oxygen. After 6 hours radiation under continuous oxygen-bubbling at between  $-37^{\circ}$  and  $-5^{\circ}\text{C}$ , 7.5 litres of oxygen have been absorbed. The reaction is stopped and after removal by distillation of the products volatile at room temperature the liquid medium appears heterogeneous. The lower liquid phase (about 25 g) is separated and gives fractions of products having boiling temperatures between  $40^{\circ}$ /760 mm and  $230^{\circ}$ /0.3 mm when distilled. The upper liquid layer gives, after removal of the carbon tetrachloride, 8 g of liquid products containing only C, F and O and having boiling temperatures between  $80^{\circ}\text{C}$  and  $210^{\circ}\text{C}$ /760 mm. Products having the same boiling temperature show characteristics completely equivalent to the corresponding products of Examples 1 and 2.

#### EXAMPLE 4

A photochemical reaction between perfluoro-propylene and oxygen is carried out in conditions analogous to those of the preceding Example, except that 275 g of methylene dichloride are used as diluent in place of carbon tetrachloride. After 6 hours reaction, the two liquid layers present in the reaction medium are separated and distilled. A total of 28 g of fluoroxygenated products are obtained, which have a distillation interval between  $45^{\circ}$ /760 mm Hg and  $250^{\circ}$ /0.6 mm Hg and properties very similar to the products of the preceding Examples.

#### EXAMPLE 5

An apparatus is prepared consisting of a cylindrical glass vessel having a capacity of 0.4 litre and provided with a thermometer and a gas inlet pipe dipping down to the bottom and connected with the atmosphere by means of a reflux condenser cooled at  $-78^{\circ}\text{C}$  and containing the ultraviolet-ray lamp. Into this vessel 460 g of perfluoro-propylene are distilled at  $-78^{\circ}\text{C}$  and a photochemical reaction is started by irradiation with ultraviolet light and feeding of a stream of 60 l/h of dry air to the liquid phase kept at  $-70^{\circ}\text{C}$ . The air leaves the reactor and is removed after passage through the condenser at  $-78^{\circ}\text{C}$ ,

which sends at least part of the entrained perfluoro-propylene back into the reactor. As the reaction proceeds, the temperature of the liquid phase rises gradually until it reaches

25°C, after about 8 hours of reaction. The liquid product remaining in the reactor, 108 g, is distilled and separated into the following fractions:

A)	5g	30—57°C/760 mm
B)	11g	45—98°C/18 mm
C)	35g	80—166°C/0.3 mm
D)	90g	166—260°C/0.3 mm
E)	25g	residue

- 10 which have characteristics completely equivalent to those of the products described in Example 1.

#### EXAMPLE 6

- 15 An apparatus is prepared consisting of a cylindrical 0.4 litre glass reactor containing an ultraviolet-ray lamp, and provided with a thermometer, a gas inlet pipe dipping down to the bottom of the vessel, a gas outlet pipe provided with a reflux condenser cooled to 20 -78°C, and an outer cooling bath. 380 g of perfluoro-propylene are introduced into the reaction by distillation at low temperature. At a temperature of -70°C and with ultraviolet radiation, the introduction through the inlet dipping pipe of 60 l/h of an anhydrous gas consisting of 2 parts by volume of oxygen

and 1 part of volume of tetrafluoroethylene is started. The gas is fed from a 150 litre gasometer by means of a circulating pump. The gas leaving the reactor through the reflux condenser is continuously recycled to the same gasometer, after washing with a potassium hydroxide solution having a concentration of 20% by weight. After 6 hours the temperature of the liquid phase has gradually risen to -27°C, a total of 52 litres of gas has been absorbed and the reaction is stopped. By heating at room temperature, 212 g of unreacted perfluoro-propylene removed from the liquid phase and 215 g of products are obtained from the reaction. The following fractions are separated by distillation:

Fraction	Weight (g)	Distillation Interval
a)	15	25—60°/760 mm
b)	9	47—105°/20 mm
c)	15	80—102°/0.5 mm
d)	22	102—154°/0.5 mm
e)	125	160—260°/0.5 mm
f)	27	260—305°/0.5 mm
g)	2	residue

- 45 Fraction f) shows a density  $d_4^{24}$  of 1.8949 and a viscosity at 24°C of 2990 centipoises, a value considerably higher than that of the fraction having an analogous distillation interval obtained by photochemical reaction of oxygen with perfluoro-propylene only.

#### EXAMPLE 7

- 50 In this example shows the possibility of obtaining a polyperoxide of perfluoropropylene

directly by reacting the olefin with oxygen in the presence of U.V. radiation having a suitable spectrum. For this purpose a low pressure mercury-vapour NK 6/20 Hanau quartz generator having an emission spectrum containing a high percentage of radiation having a wave length lower than 2,600 Å and an absorption of 8 Watt is used. This source of U.V. radiation which has a tubular shape and an outer quartz sheath, is completely immersed in 490 g of liquid perfluoro-propylene

placed in a 0.6 litre glass vessel provided with a dipping pipe for the introduction of oxygen, and a reflux condenser kept at  $-78^{\circ}\text{C}$  and which is immersed in an outer cooling bath.

5 A closed circuit is prepared for the circulation of molecular oxygen. By means of this circuit the oxygen withdrawn from a 10 litre gasometer by means of a circulating pump and dried, is fed to the reaction vessel and, when leaving the vessel through the condenser

10 at  $-78^{\circ}\text{C}$ , is washed with an aqueous potassium hydroxide solution and sent back to the starting gasometer. The reaction is started by keeping perfluoro-propylene at a temperature between  $-65^{\circ}\text{C}$  and  $-75^{\circ}\text{C}$  and by feeding through it an oxygen flow of about 50 l/h.

15 After 11 hours of reaction 2.4 litres of oxygen have been absorbed, the reaction is stopped and the unreacted perfluoropropylene is removed from the reactor by distillation  $-30^{\circ}\text{C}$ . It appears to contain about 0.3% of epoxide. 17.0 g of a liquid-semisolid product are obtained as a residue which analysis shows to contain:

25 C 19.83%; F 62.73%; O 17.44%

These figures practically correspond to the formula  $(\text{C}_3\text{F}_6\text{O}_2)_n$ .

The infrared spectrum of this compound shows that  $-\text{COF}$  groups are present by the characteristic absorption band in the zone at  $5.25 \mu$ , as shown in the accompanying drawing. The presence and the amount of these acid groups is also shown by titration of the total acidity with a cold alkaline solution and determination of the amount of fluoride thus hydrolysed. The presence of peroxidic groups is clearly demonstrated by the product, which when treated with an acid solution, for example an acetic anhydride solution, of an alkali metal iodide, releases a substantial amount of iodine. 200 mg of the product are dissolved in 5 cc of 1,1,2-trifluorotrichloroethane ( $\text{CF}_2\text{Cl}-\text{CFCl}_2$ ). To this solution are added 20 cc of acetic anhydride containing

45 2 g of potassium iodide and the mixture is stirred for a few minutes and titrated with 0.1 N sodium thiosulphate. 19.95 cc were used, corresponding to 0.9 atoms of active oxygen per perfluoro-propylene ( $\text{C}_3\text{F}_6$ ) unit.

50 The polyperoxide of perfluoropropylene thus obtained is remarkably stable at room temperature. When heated in the pure state to a temperature higher than  $70-80^{\circ}\text{C}$ , it decomposes in a violet manner developing gaseous or low-boiling products and leaving practically no liquid residue. More controllable decomposition of the polyperoxide can be achieved by operating on solutions of the compound in solvents such as perfluorodimethylcyclobutane, or 1,1,2-trifluorotrichloroethane.

60

Solutions of the polyperoxide in these solvents can be used for the usual transformation reactions of the terminal  $-\text{COF}$  groups for

example hydrolysis, esterification, salt or amide formation reactions which make it possible to obtain a number of derivatives.

A solution of 10 g of polyperoxide in 100 cc of perfluorodimethylcyclobutane is irradiated, at  $-25^{\circ}\text{C}$  to  $-10^{\circ}\text{C}$ , with an immersed U.V. radiation source, consisting of a high-pressure mercury-vapour Q 81 Hanau quartz generator having an absorption of 70 Watts. The spectral energy distribution of this generator is such that the ratio of the energy of the U.V. radiation emitted with a wave length higher than  $3,000 \text{ \AA}$  to the energy of the radiations emitted with a wave length lower than  $2,700 \text{ \AA}$  is 6.66:1. The irradiation is continued for 5 hours during which a slow dry nitrogen flow is bubbled through the liquid phase. At the end of the operation the solvent is distilled off under reduced pressure and an oil is recovered which is acid and has a percentage composition practically corresponding to the formula  $(\text{C}_3\text{F}_6\text{O}_{1.05})_n$ . This product is stable to heating and can be distilled up to about  $300^{\circ}\text{C}$  under a pressure of 1 mm Hg. The presence of peroxidic groups cannot be detected. This shows that the action of suitable U.V. radiations makes it possible to transform a peroxidic compound into a stable compound having a lower oxygen content.

#### EXAMPLE 8

With the apparatus described in the preceding Example a photochemical reaction is carried out between liquid perfluoro-propylene (525 g) and molecular oxygen, by irradiation at a temperature of about  $-60^{\circ}\text{C}$  to  $-50^{\circ}\text{C}$ . After 18 hours 2.65 normal litres of oxygen are absorbed and the reaction is stopped. From the reaction apparatus kept at  $-78^{\circ}\text{C}$  under an anhydrous atmosphere a sample of 14 cc of solution is withdrawn and by evaporating off unchanged perfluoro-propylene a polyperoxidic product completely similar to that described in the preceding Example is obtained as a residue.

The high pressure mercury-vapour U.V. generator is immersed in the reactor and, while feeding a slow nitrogen flow to the solution at about  $-40^{\circ}\text{C}$ , the solution is irradiated for 1 hour. A 23 cc sample of solution is withdrawn. After evaporating off unchanged perfluoro-propylene from this sample, as the residue an oil is obtained which appears to have a low periodic oxygen content and is remarkably stable to heating up to temperatures of about  $200^{\circ}\text{C}$ . The residue of the solution of the initial polyperoxide in perfluoropropylene is subjected to irradiation for a further 6 hours and then perfluoropropylene is removed by distillation. As the residue, 24 g of a liquid having the following composition: C = 21.69%, F = 68.20%, O = 10.11% corresponding to the formula  $(\text{C}_3\text{F}_{6.07}\text{O}_{1.05})_n$ , are obtained. This compound, on reaction with an acid solution of an alkali metal iodide,

reveals the presence of practically no peroxidic groups. In the infrared spectrum the absorption bands of  $\text{—COF}$  and  $\text{—COOH}$  groups are present. By titration with an alkaline solution and determination of the amount of fluoride hydrolysed, an average equivalent weight of about 2,411 is determined. The compound is remarkably stable to heat, it can be distilled between  $50^\circ\text{C}$  under atmospheric pressure and  $250^\circ\text{C}$  under 1 mm Hg. The distillation curve is continuous and the biggest fraction by weight is distilled between  $80^\circ\text{C}$  and  $110^\circ\text{C}/1$  mm Hg.

#### EXAMPLE 9

Under the reaction conditions of Example 1 but at  $29^\circ\text{C}$  and with a molecular oxygen flow of 20 lh, a photochemical oxidation of 505 g of perfluoro-propylene is carried out for 22 hours. At the end of the reaction, by distillation of the unreacted olefin, 71 g of a liquid acid product having a high viscosity at room temperature and a percentage composition corresponding to the formula  $(\text{C}_3\text{F}_6\text{O}_{1.6})_n$  are obtained. 300 mg of this product are iodometrically titrated as in Example 7: 18.85 cc of 0.1 N thiosulphate are used, which corresponds to 0.55 atoms of active oxygen per  $\text{C}_3\text{F}_6$  unit. This product shows an acidimetric equivalent weight of  $1 \times 10^3$ , determined by prolonged agitation of a sample with a cold 0.1 N sodium hydroxide solution and a back titration of the unreacted excess alkali and of the hydrolysed fluoride of the  $\text{—COF}$  groups. A sample of 10 g of product, on gradual heating up to a temperature of  $130^\circ\text{C}$  develops gaseous products and leaves, as a residue, 2.5 g of a liquid which is very stable to the further action of heat up to above  $350^\circ\text{C}$ , has a composition corresponding to the formula  $(\text{C}_3\text{F}_6\text{O}_{1.66})_n$  and, by treatment with an acid solution of an alkali metal iodide, does not show any tendency to act as an oxidizing agent. This example shows that, by varying some conditions with respect to those described in Example 7 (particularly increasing the irradiation time and reaction temperature), it is possible to obtain products having an intermediate composition between that of a polyperoxide and a polyether of perfluoro-propylene.

#### EXAMPLE 10

This Example shows that, by using a source emitting U.V. radiation with a wide spectrum, and an experimental system which makes it possible quickly to remove the reaction product from the reactor in which the photochemical reaction of perfluoro-propylene with oxygen is carried out, it is possible to operate continuously. Thus it is possible to obtain polymeric perfluorooxygenated liquids which have a higher oxygen content than a pure polyether having the formula  $(\text{C}_3\text{F}_6\text{O})_n$ .

For this purpose an apparatus is prepared which comprises a reactor as such, which is a

0.5 litre glass reactor containing a liquid phase of perfluoro-propylene, in which a Q 81 Hanau high-pressure mercury-vapour U.V. radiation generator is immersed. A dipping pipe on the bottom of the reactor allows the introduction of an oxygen flow which then leaves the reactor through a condenser kept at  $-78^\circ\text{C}$ . The unreacted oxygen is washed with an alkaline solution and sent into a 50 litre gasometer from which, by means of a circulating pump, it is continuously introduced, after drying, into the photochemical reactor. The oxygen consumed in the reaction is periodically replaced in the cycle. To the photochemical reactor a perfluoro-propylene flow is also continuously fed from a 50 litre gasometer and recycled by means of a circulating pump. The level of the liquid phase in the reactor is kept constant by a continuous discharge through the bottom of a corresponding amount of liquid which is sent to a continuous system of fractional distillation. From this system the olefin and the compounds, if any, boiling below  $20^\circ\text{C}$ , are sent back in the gaseous state to the gasometer and the liquid reaction products are collected separately. The reacted perfluoro-propylene is periodically replaced in the cycle.

Reaction is carried out by initially introducing into the reactor 600 g of perfluoro-propylene and by feeding to it at  $-35^\circ\text{C}$  to  $-30^\circ\text{C}$  an oxygen flow of 80–100 l/h hour and a perfluoro-propylene flow of about 100 l/h. After 42 hours of reaction 330 normal litres of oxygen are absorbed and 2,850 g of polymeric liquid products are obtained.

Analysis of the residual perfluoro-propylene in the cycle shows that it contains 22.2% by weight of epoxide  $(\text{C}_3\text{F}_6\text{O})$ , corresponding to a production of 190 g of epoxide. The liquid product has the following average composition: C = 21.14%; F = 66.93%; O = 11.93% corresponding to the formula  $(\text{C}_3\text{F}_6\text{O}_{1.27})_n$ . This product releases iodine on contact with an acid solution of an alkali metal iodide and has a remarkably acid reaction. 500 mg of this product are iodometrically titrated as in Example 7: 13.55 cc of 0.1 N thiosulphate are used, which corresponds to 0.23 atoms of active oxygen per  $\text{C}_3\text{F}_6$  unit. In the infrared absorption spectrum the characteristic bands at  $5.25 \mu$ , due to the presence of  $\text{—COF}$  groups, are present. A weighed sample of product is reacted with a standard aqueous alkali solution, with agitation. The excess alkali is back titrated with an acid and in the neutral solution the amount of fluoride obtained by hydrolysis of the  $\text{—COF}$  groups is determined. The product has an acidimetric equivalent weight between 1,300 and 1,400. These values have only an approximate character due to the complex constitution of the mixed liquid product and to the difficulty of carrying out titrations in a non-homogeneous medium. These polymeric liquid products in fact, by treatment with alkali solutions, give

the corresponding salts, some of which (those having a relatively low molecular weight) are soluble in water and some are insoluble and have the appearance of soaps, having clearly emulsifying properties.

- 5 A sample of the product is subjected to distillation: about 30% of the product distills at between 40°C under atmospheric pressure and 175°C under 1 mmHg/ about 65% distills at  
10 between 175°C under 1 mmHg and 360°C under 1mmHg while the remaining about 5% distills only at higher temperatures. The infrared absorption spectra of the various fractions are practically coincident while the acidimetric  
15 equivalent weight, the viscosity and density progressively increase as the boiling temperature of the mixture increases. The average composition of the fraction distilled between 175°C/1 mmHg and 360°C/0.1 mmHg  
20 appears to correspond to the formula  $(C_3F_6O_{1.1})_n$ . A sample of 200 g of the obtained product is irradiated at a temperature of 20 to 30°C for 100 hours with a high-pressure mercury-vapour U.V. light source.  
25 During this treatment a slow dry nitrogen flow keeps in agitation the liquid phase in which the U.V. lamp is immersed. At the end of this treatment the sample shows a weight loss of 5% while its average percentage composition now corresponds to the formula  
30  $(C_3F_6O_{1.19})_n$ . While the oxidizing power of the product after irradiation becomes remarkably lower, the other characteristics, including the distillation curve, do not show remarkable  
35 changes. Similar results have been obtained by subjecting a sample of the product to heating at the temperature of 380°C for 30 hours, in an autoclave in which the pressure was kept below 40 atmospheres. The product after this

thermal treatment has a composition corresponding to the formula  $(C_3F_6O_{1.15})_n$ .

From the acid products obtained as described above and having a certain content of peroxidic groups, by suitable treatments at is possible to obtain neutral products having a very high thermal and chemical stability. Such a suitable treatment may consist of a neutralization with alkali and thermal decomposition of the salts, which eliminates the carboxylic acid groups and most of the peroxidic bridges. 600 g of potassium hydroxide (85%) in the form of tablets are introduced into a 3 litre vessel provided with an agitator, a reflux condenser and a charge pipe. The vessel is heated to 100°C and the slow introduction of the crude oil is started with vigorous agitation. The temperature rises to 130—140°C while the introduction of 2.0 kg of fluoro-oxygenated product is carried out in 6 hours. The salt formed is kept in agitation for further 24 hours at about 140°C. By eliminating the circulation of water from the reflux condenser, the water contained in the vessel is left to distil together with a small fraction of neutral low boiling fluoro-oxygenated oils while the inner temperature rises to 320 to 330°C. During this stage there is observed also the development of a remarkable amount of gas, mainly carbon dioxide. After a further 4 hours of heating to 300 to 320°C, the contents of the reactor are cooled and the oil previously steam-distilled is added and all the liquid contained is filtered to remove the solid salts which prevailing consist of potassium fluoride. In total 1,350 g of neutral fluorinated oils are obtained which by distillation are fractionated into the fractions having the characteristics reported in the following Table.

Fraction	Distillation Range	g	Composition	Average Molecular Weight
I	50—100°C/1 mmHg	460	$C_3F_6O_{1.00}$	600—1,000
II	100°/0.1 mm to 200°C/0.1 mm	555	$C_3F_6O_{1.05}$	1,000—2,000
III	200°C/0.1 mm to 350°C/0.05 mm	300	$C_3F_6O_{1.03}$	2,500—3,500
IV	residue	30	$C_3F_6O_{1.02}$	>5,000

- 80 All these fractions have no oxidizing power and are exceptionally chemically stable. In the infrared absorption spectrum of these products the presence of bands characteristic of acid groups cannot be observed.

#### 85 WHAT WE CLAIM IS:—

1. A process for the preparation of products containing  $-C_3F_6-O-$  and  $-C_3F_6-O-O-$

units, either alone or with  $-C_2F_4-O-$  and  $-C_2F_4-O-O-$  units, distributed at random in a polymer chain which comprises subjecting perfluoro-propylene or a mixture thereof with tetrafluoro-ethylene in the liquid phase to a photochemical reaction with molecular oxygen at between  $-100^\circ\text{C}$  and  $+25^\circ\text{C}$ , at a pressure between 0.1 and 10 atmospheres absolute in the presence of ultra-violet radiation.

2. A process according to Claim 1 which is carried out at from  $-80^{\circ}\text{C}$  to  $0^{\circ}\text{C}$ .
3. A process according to Claim 1 or Claim 2 which is carried out at from 0.2 to 5 atmospheres absolute.
4. A process according to any of the preceding Claims in which the reaction between perfluoro-olefin(s) and oxygen is carried out in the presence of a liquid or gaseous diluent.
5. A process according to Claim 4, wherein as a gaseous diluent nitrogen is used.
6. A process according to Claim 4, wherein as a liquid diluent a perfluoroparaffin having the general formula  $\text{C}_n\text{F}_{2n+2}$ , in which  $n$  is between 3 and 12, perfluorocyclobutane, perfluorocyclohexane, perfluorodimethylcyclobutane, perfluorobenzene, a perfluoroamine, a perfluoro-fatty acid having from 2 to 10 carbon atoms in the molecule, cyclic and open chain perfluoro-ethers, carbon tetrachloride, chloroform, methylene dichloride, methylchloroform or a fluorochloro derivative of methane, ethane, or propane is used.
7. A process for the preparation of perfluoro-olefin products substantially as hereinbefore described in any of the Examples.
8. Perfluoro-olefin products prepared by a process according to any of the preceding Claims.

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1 SHEET

COMPLETE SPECIFICATION

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